Characterization of Precursor-Derived Silicon-Carbon-Nitrogen Ceramics after Creep Testing

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Precursor-derived Si-C-N ceramics after creep testing in air were characterized using X-ray diffractometry (XRD) and transmission electron microscopy (TEM). XRD analysis showed that the crept Si-C-N ceramics were covered by an α -cristobalite layer. TEM observations revealed that the precipitated nanocrystallites in the crept Si-C-N ceramics were β -SiC. Between α -cristobalite and crept Si-C-N ceramic, there was an intermediate zone in which Si₂N₂O nanocrystallites were distributed homogeneously. Moreover, Si₂N₂O nanocrystallites were often found covering the surface of nanosized gas channels in the crept Si-C-N ceramics, where no α -cristobalite phase was detected. Based on these observations, a two-step oxidation mechanism of Si-C-N ceramics during creep testing in air was proposed.

I. Introduction

PRECURSOR-DERIVED Si-C-N ceramics have been extensively studied during past years because of their high thermal stability, oxidation, and creep resistance. On creep testing in air, crystallization and oxidation processes proceed concomitantly in the amorphous Si-C-N ceramics. Bill et al.1 have reported that, after creep testing in air at 1550°C, nanosized Si₃N₄ crystallites and free carbon phases are observed precipitating in the amorphous Si-C-N ceramics derived from polyvinylsilazane and polyhydridomethylsilazane; in addition, a SiO₂ surface layer is found covering the crept Si-C-N ceramics. Riedel et al.² have revealed that the oxidation process of precursor-derived Si-C-N ceramics is diffusion controlled, despite an early reaction-controlled stage. As a consequence, the Si-C-N ceramics are protected from further oxidation because of the low diffusion coefficient of oxygen and nitrogen in SiO₂. It is generally accepted that the interface between ceramic and SiO₂ is important in the diffusion process during oxidation. However, until now, only a few investigations have been devoted to the characterization of the interfacial structure between SiO₂ and precursor-derived ceramics. Mocaer et al.³ have claimed that there is no intermediate layer between SiO₂ and Si-C-N-O filaments, at least at a scale larger than ~ 10 nm. Baldus and Passing⁴ have observed that a complex BN(O)-SiO₂ double layer is formed during oxidation of an SiBCN fiber. Recently, Cinibulk and Parthasarathy⁵ have substantiated that, in an oxidized polymer-derived SiBCN fiber, there are four distinct zones: (i) a surface layer of α -cristobalite, (ii) a homogeneous layer of amorphous SiO₂, (iii) a mixed layer of SiBCNO glass with BN

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II. Experimental Procedures

The Si-C-N ceramics studied here were derived from a commercial polysilazane (KiON Corp., Columbus, OH). The asreceived precursor was first crosslinked under an argon atmosphere at a temperature of ~250°C for 2 h. After the precursor was ball-milled and sieved, a crosslinked polymer powder resulted. The powder was then compacted in a graphite die at a uniaxial pressure of 48 MPa and temperatures of 150°-400°C. Finally, the compacted material was thermolyzed at 1050°C for 2 h in argon atmosphere with the conversion of polymer to ceramic. After the material was thermolyzed, the chemical composition of Si-C-N ceramics was determined as SiC_{0.97}N_{0.85} (residual oxygen of O_{0.02}). Before they were creep-tested, the amorphous Si-C-N ceramics were annealed in argon atmosphere at 1400°C for 5 h.

The creep specimens, with a height of 4.5 mm and a crosssectional area of 1.7 mm \times 1.7 mm, were cut from the annealed monoliths, which contained \sim 12% open porosity. The compression creep tests were performed in air at 1400°C for 235 h and at 1500°C for 238 h, using an applied stress of 100 MPa. The equipment and procedure of creep testing have been described elsewhere.⁶

After they were creep-tested, the crept Si-C-N bulk specimens were cross sectioned into halves. One half was used for X-ray diffractometry analysis (XRD; Model D5000 Kristalloflex, Siemens, Karlsruhe, Germany), using CuK α_1 radiation ($\lambda = 1.5406$ Å). The other half was used for transmission electron microscopy study (TEM; Model 4000FX, JEOL, Tokyo, Japan). TEM foil preparation followed standard techniques, which involved diamond cutting, ultrasound drilling, mechanical grinding, dimpling, polishing, and argon-ion thinning to perforation. Final thinning of the sample was performed using a precision ion-polishing system (PIPS; Gatan, Inc., Pleasanton, CA) by mounting on a copper ring with a central hole of 1500 μ m.

III. Results and Discussion

As reported earlier,¹ XRD analysis here (Fig. 1) also reveals that the surface of Si-C-N ceramics is covered by an α -cristobalite layer after creep testing in air. Besides α -cristobalite peaks, no other special features can be determined from the XRD curves. To examine the detailed structure of crept Si-C-N ceramics, TEM, including bright-field (BF) imaging, dark-field (DF) imaging, and selected-area diffraction (SAD) techniques, is used. A typical DF-TEM micrograph taken from the crept Si-C-N ceramic specimen at 1400°C is shown in Fig. 2. It is evident that there are many nanocrystallites precipitating homogeneously in the amorphous

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Fig. 1. XRD measurements of precursor-derived Si-C-N ceramics after creep testing in air.

matrix. SAD analysis reveals (inset of Fig. 2) that the precipitated nanocrystallites are β -SiC, whose *d* spacings of (111), (220), and (311) are 0.253, 0.154, and 0.132 nm, respectively. This result is derived from the fact that the *d* spacings of (111), (220), and (311) in β -SiC are in concordance with three diffraction halos in the SAD pattern at 3.95, 6.49 and 7.58 nm⁻¹, respectively. Previous investigations also have revealed that annealing of Si-C-N ceramics at 1400°C in nitrogen atmosphere results in β -SiC nanocrystallites precipitating homogeneously in the amorphous matrix,^{7,8} indicating that the crystallization behavior of Si-C-N ceramics does not significantly change during creep testing in air as compared with an annealing treatment in nitrogen.

During observation, the α -cristobalite phase is prone to become amorphous under the electron beam after exposure for a minute or so. This phenomenon also has been reported in an earlier study on air heat-treated SiC Nicalon fibers by Maniette and Oberlin.⁹ Figure 3 shows a typical interfacial structure between α -cristobalite and crept Si-C-N ceramics, where the α -cristobalite phase provides a weak contrast in BF and DF images because of its tendency to become amorphous. By contrast, many homogeneously distributed nanocrystallites (white spots in Fig. 3(a) and dark spots in Fig. 3(b)) can be clearly seen on the other side. At first sight, these nanocrystallites are considered as β -SiC because of their similar size, distribution, and homogeneity. However, SAD analysis (inset of Fig. 3(a)) reveals that these nanocrystallites



Fig. 2. DF-TEM micrograph showing the microstructure of unoxidized Si-C-N ceramics after creep testing in air at 1400°C; inset is the corresponding SAD pattern.

are neither SiC nor Si₃N₄, because the diffraction spots in the SAD pattern cannot be indexed by the crystallographic data of SiC and Si₃N₄. Instead, they all can be indexed by the crystallographic data of Si₂N₂O (space group *Cmc*21; lattice parameters of a = 0.884nm, b = 0.547 nm, and c = 0.484 nm), whose atomic lattice planes are labeled in the SAD pattern. This finding indicates that, adjacent to the SiO₂ surface layer, there exists an intermediate zone in which many Si₂N₂O crystals precipitate homogeneously. Moreover, the diffuse halo in the SAD pattern substantiates the presence of an amorphous matrix, whose chemical composition is definitely different from $SiC_{0.97}N_{0.85}$, because there are two opposite diffusion fluxes (O2 and N2, CO) through this zone during oxidation. An intermediate Si₂N₂O zone adjacent to SiO₂ surface layer also has been found in an oxidized, chemically vapor deposited (CVD) $\alpha\mbox{-}Si_3N_4,^{10}$ in which the molecular oxygen diffusivities (depending on the temperature) are calculated to be 1-3 orders of magnitude lower than those in SiO₂.¹¹ Thus, the formation of Si₂N₂O must be important in the oxidation resistance of Si-C-N ceramics during creep testing in air.



Fig. 3. TEM micrographs showing the interfacial structure between α -cristobalite and crept Si-C-N ceramic: (a) DF image (inset is the SAD pattern acquired from the ceramic side) and (b) BF image.



Fig. 4. (a) BF-TEM micrograph showing the microstructure of nanosized gas channels in the crept Si-C-N ceramic at 1500°C and (b) corresponding SAD pattern.

Based on the observation that nanosized Si_2N_2O crystals form between SiO_2 and crept Si-C-N ceramic, a two-step oxidation model of Si-C-N ceramics during creep testing in air is proposed as follows:

$$4\text{SiC}_{0.97}\text{N}_{0.85}(s) + 2.94\text{O}_2(g) \rightarrow 2\text{Si}_2\text{N}_2\text{O}(s) + 3.88\text{CO}(g)$$

$$+ 1.7N_2(g)$$
 (1)

$$2\operatorname{Si}_{2}\operatorname{N}_{2}\operatorname{O}(s) + 3\operatorname{O}_{2}(g) \to 4\operatorname{SiO}_{2}(s) + 2\operatorname{N}_{2}(g)$$
(2)

According to this model, the Si-C-N ceramic is first oxidized to form the $Si_2N_2O(s)$ phase, and further oxidation results in the transformation of $Si_2N_2O(s)$ to $SiO_2(s)$. If there is not enough oxygen available, the oxidation process stops at the first stage. To substantiate this hypothesis, it is necessary to find an area where only Si₂N₂O phase covers the surface of crept Si-C-N ceramics. It is known that, besides the outer surface of crept Si-C-N ceramics, the surface of accessible inner gas channels is also oxidized during creep testing. Moreover, the oxidation products always block smaller gas channels and protected inner parts from further oxidation. Therefore, it is more likely to find the requested area at the surface of nanosized gas channels. Figure 4(a) is a BF-TEM micrograph taken from the crept Si-C-N ceramic specimen at 1500°C. There are three nanosized gas channels whose surfaces are covered by many nanosized crystals. SAD analysis (Fig. 4 (b)) documents that all these crystals can be attributed to the Si₂N₂O phase, while no cristobalite can be detected. This finding provides sound evidence to support the two-step oxidation mechanism of Si-C-N ceramics during creep testing in air.

IV. Conclusions

After they are creep-tested in air, the precursor-derived Si-C-N ceramics form three different zones. The first (outer) zone is the well-known SiO₂ surface layer, composed of α -cristobalite. The second zone, adjacent to the SiO₂ surface layer, is an intermediate

zone in which many nanosized Si_2N_2O crystals are distributed homogeneously. The third zone is the virgin Si-C-N ceramic, where many β -SiC nanocrystallites have precipitated homogeneously. The surface of nanosized gas channels is always covered only by Si_2N_2O nanocrystallites, proving that a two-step oxidation process occurs in the crept Si-C-N ceramics. Accordingly, the superior oxidation resistance of Si-C-N ceramics is attributed to the SiO₂ surface layer and to the intermediate Si₂N₂O-rich zone.

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